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COMPARISON ASSAY OF A GOLD PLATING SOLUTION BY
CONTROLLED-POTENTIAL COULOMETRY AND FIRE ASSAY

J. E. Harrar
M. C. Waggoner
J. W. Loy

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J. E. Harrar, M. C. Waggoner, and J. W. Loy

Lawrence Livermore National Laboratory
Livermore, CA 94550

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ABSTRACT

A commercial gold-electroplating solution was assayed for its total gold content by two high-precision techniques and the results were compared. The solution was analyzed using controlled-potential coulometry at the authors' laboratory and by the fire assay technique at Metallurgical Laboratories, Inc., of San Francisco. Agreement between the two laboratories was within 0.3% for the total quantity of gold in two containers that were sampled, and within 0.5-1.0% for the concentrations of gold in the solutions.

INTRODUCTION

For over a decade an analytical method involving an acid boil down and controlled-potential coulometry has been used to assay various gold and silver-bearing materials at the Lawrence Livermore National Laboratory (LLNL).¹ The technique of coulometry itself is capable of excellent precision and accuracy; nevertheless, it has remained relatively unknown in the precious metal industry. For this reason we have recently written a paper² (to be published in the near future), which describes our procedures and the results of several tests of the accuracy of the methods by means of the standard addition technique.

Although the accuracy of the coulometric determination of gold has been verified many times with metallic standards³ in comparison with other laboratories, and in comparison with the fire assay,⁴ no direct comparisons with the fire assay have been performed for the more complicated electroplating formulations, where coulometry requires sample pretreatment by the acid boil-down procedure.² Since we are now using this procedure for monitoring all incoming shipments of salts and solutions, we decided to carry out a comparison of our method with one involving fire assay as performed by a commercial testing laboratory.

Two containers of a sulfite-based, gold-bath replenisher solution were sampled; each was purchased to contain a total of exactly 2 troy ounces of gold in a volume of solution of approximately 800 ml. We employed our usual procedures of sampling the container volumetrically and measuring the total solution volume by means of a 1-l graduated cylinder. The commercial testing laboratory, Metallurgical Laboratories, Inc., of San Francisco, elected to carry out the assay on a weight basis. This did not afford the best comparison of the procedures as far as the measurements of the concentration of gold was concerned, but it did give a very useful comparison of the measurements of the principal quantity of interest--the amount of gold in each container.

PROCEDURES

For the analysis at LLNL, the solutions were sampled directly into the 250-ml boil-down flasks² using a calibrated, 5-ml, class A pipet. Each solution was sampled three times. In addition, to provide an indication of the effect of pipetting on the results, the solutions were also sampled using a calibrated, 1000- μ l, to-contain micropipet that was rinsed out twice after delivery. These samples were then processed in the usual manner²; for coulometry, aliquots of the diluted solution were 1000 μ l and 5-ml for the two original sample volumes. To measure the total volume of solution in each container, the solution was poured out into a Pyrex 1-l graduated cylinder. The cylinder was calibrated with water at the 1000-ml mark and found to be within 1 ml; readability in this measurement was estimated to be within ± 2 ml.

For the analysis at Metallurgical Laboratories, the weight of solution delivered by a 5-ml pipet was first ascertained by a quadruplicate determination; then each solution to be analyzed was sampled four times into the fire assay crucibles using this pipet. In addition, an estimate of the volume delivered by this pipet was obtained by a separate measurement of the density of the solution using a 50-ml pipet. The net weight of solution in each original container was found after emptying; the total quantity of gold in each container was then calculated from the fire assay value, the weight of a 5-ml sample, and the net weight of solution.

RESULTS AND DISCUSSION

The results of the analyses of the two solutions are summarized in Tables 1 and 2. In spite of the rather disparate techniques and different personnel involved, there is excellent agreement in the total quantities of gold estimated to be present. Agreement in the estimated concentrations of gold, which more directly indicates agreement between the boil-down/coulometry technique and the fire assay technique, is not as good but is still very satisfactory. This experiment was only a partial comparison of the two techniques, however, because different analysts used different pipets and slightly-different techniques in the sampling.

In the test of the effect of pipet size in the LLNL sampling, there was a significant effect (higher results when the micropipet was used) in the case of solution A but not solution B. Again, however, pipet volume was not strictly the only variable being tested; the quantity of gold handled in the acid boil-down was ~380 mg with the 5-ml sample and one-fifth of that with the 1000 μ l sample.

In conclusion, it appears that our gold assay procedures, which are based on volumetric techniques, are at least as accurate and precise as the more traditional fire assay for monitoring these solutions.

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Table 1. Analysis of electroplating Solution A for gold.

5 ml aliquot per determination except as noted.

Measured total volume = 791 ml

Measured total net weight = 1005 g

Metallurgical Laboratories			LLNL	
Concentration		Total Au, tr. oz.	Concentration	Total Au,
mg Au/g soln.	mg Au/ml soln.		mg Au/ml soln.	tr. oz.
60.81			77.58	
60.87			77.58	
61.16			77.58	
<u>60.92</u>				
Mean	60.94	76.87	77.58	<u>1.973</u>
Std. Dev.	0.15	0.005	0.00	0.0000
			77.72 ^a	
			77.72	
			<u>77.70</u>	<u>1.976</u>
			Mean	77.71
				0.0003
			Std.Dev.	0.012

^a1-ml aliquot per determination.

Table 2. Analysis of electroplating Solution B for gold.

5 ml aliquot per determination except as noted.
 Measured total volume = 791 ml
 Measured total net weight = 1002 g

Metallurgical Laboratories			LLNL	
Concentration		Total Au, tr. oz.	Concentration	Total Au, tr. oz.
mg Au/g soln.	mg Au/ml soln.		mg Au/ml soln.	
60.39 ^a			77.34	
61.06			77.40	
61.19			77.40	
60.94				
Mean	61.06	77.02	77.38	1.968
Std. Dev.	0.13	0.004	0.035	0.0009
			77.50 ^b	
			77.40	
			77.32	
			Mean	77.41
				1.969
			Std.Dev.	0.090
				0.0023

^aResult rejected as outlier

^b1-ml aliquot per determination

REFERENCES

1. J. E. Harrar and M. C. Waggoner, Chemical and Statistical Analysis of an Inventory of Precious Metal in the LLL Metal Finishing Shop, Lawrence Livermore National Laboratory, Livermore, CA, Rept. UCRL-51947 (1975).
2. J. E. Harrar and M. C. Waggoner, Precious Metal Analysis by Controlled-Potential Coulometry, Lawrence Livermore National Laboratory, Livermore, CA, Preprint UCRL-84217 Rev. 1 (1980); accepted by Plating and Metal Finishing.
3. J. E. Harrar and F. B. Stephens, J. Electroanal. Chem. 3, 112 (1962).
4. "Determination of Gold by Controlled-Potential Coulometry," Application Brief G-1, Princeton Applied Research Corp., Princeton, N. J., 1975.